

# **The Role of Surface Chemistry and Bulk Properties on the Cycling and Rate Capability of Lithium Positive Electrode Materials**

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**Project ID ES084**

# Overview

## Timeline

- Start date: April 2010
- End date: May 2011 - renewing
- Percent complete:  
- project on-going

## Budget

- Total Project Funding: \$945K
- FY10 funding: \$315K
- FY09 funding: \$315K
- FY08funding: \$315K

## Barriers

- High cost
- Low energy density
- Poor cycle and calendar life
- Abuse tolerance limitations

## Partners

- Lead PI: Yang Shao-Horn
- Co-PI: Azzam Mansour (NSWC)
- Collaborators: Michael M. Thackeray (ANL)

## **Research Objectives:**

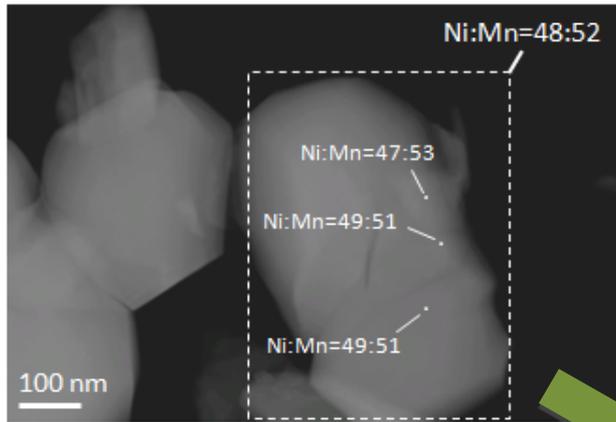
- To develop fundamental understanding of surface chemistry and bulk cation distributions on cycling performance and rate capability
- To design positive electrodes with stable electrode-electrolyte interface with improved cycling performance and rate capability

## **Research Approaches:**

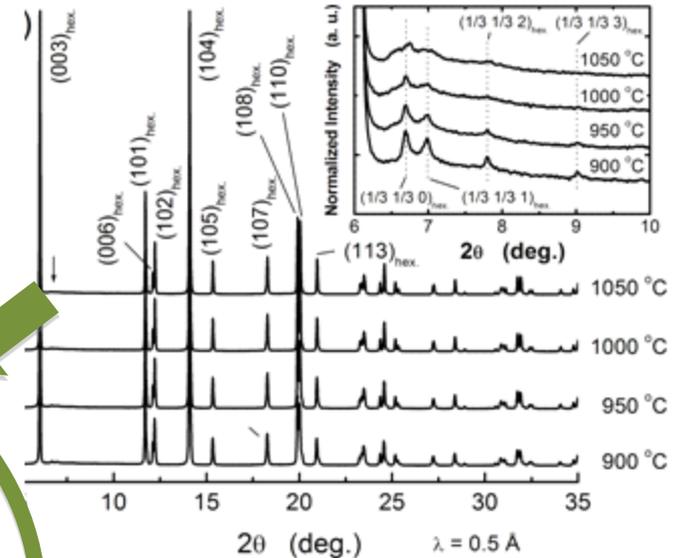
- Probing the surface chemistry of positive electrode materials before and after cycling using surface-sensitive electron microscopy, X-ray photoelectron spectroscopy and electron-yield X-ray adsorption spectroscopy.
- Studying the bulk structure of positive electrode materials before and after cycling using synchrotron X-ray diffraction and transmission X-ray absorption spectroscopy.
- Correlating surface chemistry and bulk structure information with electrochemical performance characteristics such as capacity retention and rate capability to determine the origin of surface instability.

# Research Approach Overview

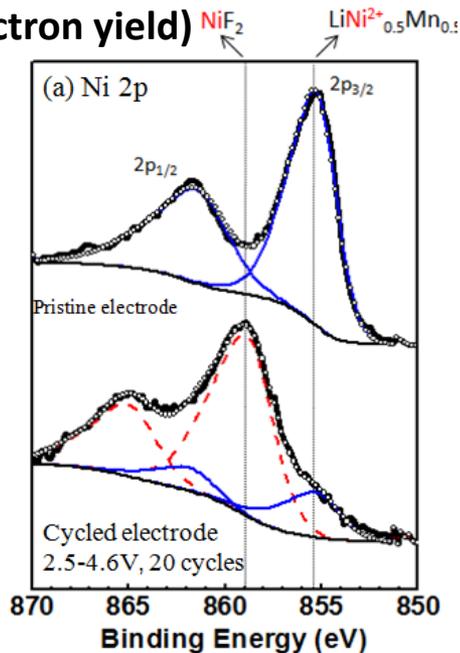
**Surface and Bulk Chemistry:** Electron microscopy



**Bulk Structure:** Synchrotron X-ray diffraction & X-ray absorption spectroscopy (transmission)



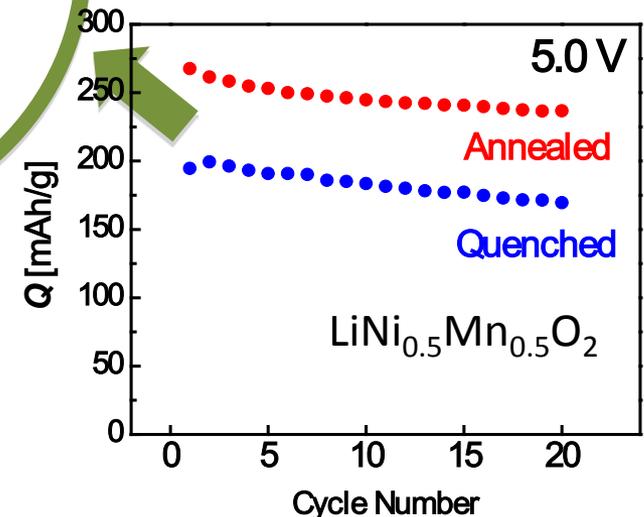
**Surface Chemistry:**  
X-ray photoelectron spectroscopy (XPS)  
X-ray absorption spectroscopy (electron yield)



Determine the origin of surface instability & bulk degradation

Design materials with improved cycling and rate capability

**Electrochemical Reactivity:**



# Milestones FY10

Develop fundamental understanding in the relationship between the surface chemistry of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  (ref.  $\text{LiCoO}_2$ ) and rate/cycle characteristics - completed

Apply the fundamental understanding to design and develop stable surfaces of cycled high-energy cathodes - completed

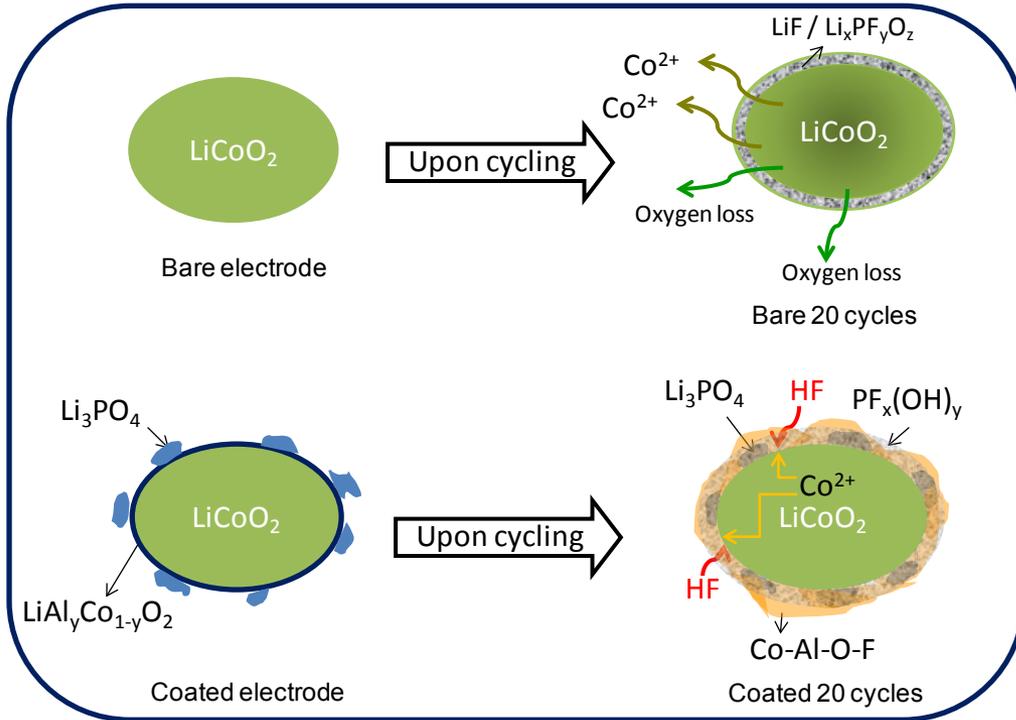
Develop angle resolved X-ray photoelectron spectroscopy (ARXPS) to study the surface chemistry of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiCoO}_2$  as a function of depth from surface - completed

Survey, synthesize and test select Li-rich  $(\text{Li}_2\text{O})_x(\text{MO}_2)_y$  (where M = Mn, Co, Ni, etc.) layered compounds – ongoing

Collect and analyze XPS and TEM data to study the surface chemistry changes of select Li rich  $(\text{Li}_2\text{O})_x(\text{MO}_2)_y$  during charge and discharge – to be performed

# Identify the working principle of surface coatings on cathode

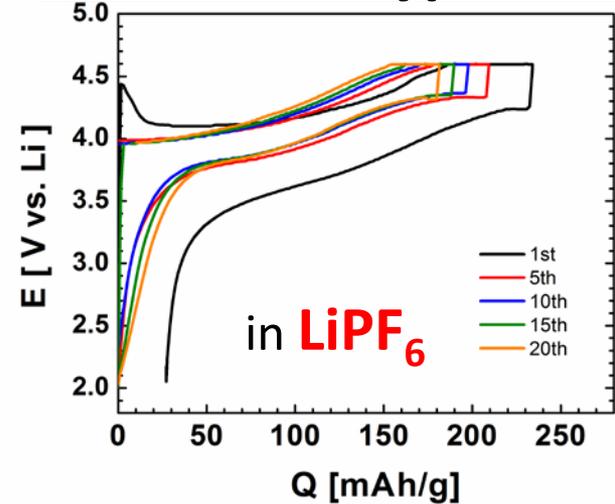
## Proposed Mechanism



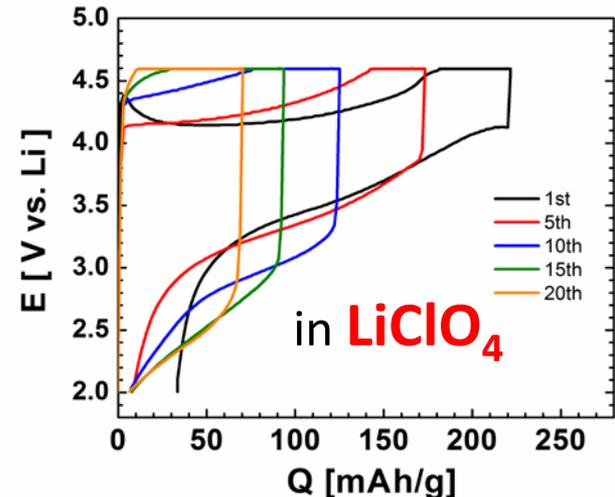
Shao-Horn et al, CM 2009

- Formation of metal fluorides/oxyfluorides at the interface is key to achieve long cycle life and high efficiency
- Coating does not enhance capacity retention in  $\text{LiClO}_4$ -based electrolyte

## Test of the hypothesis

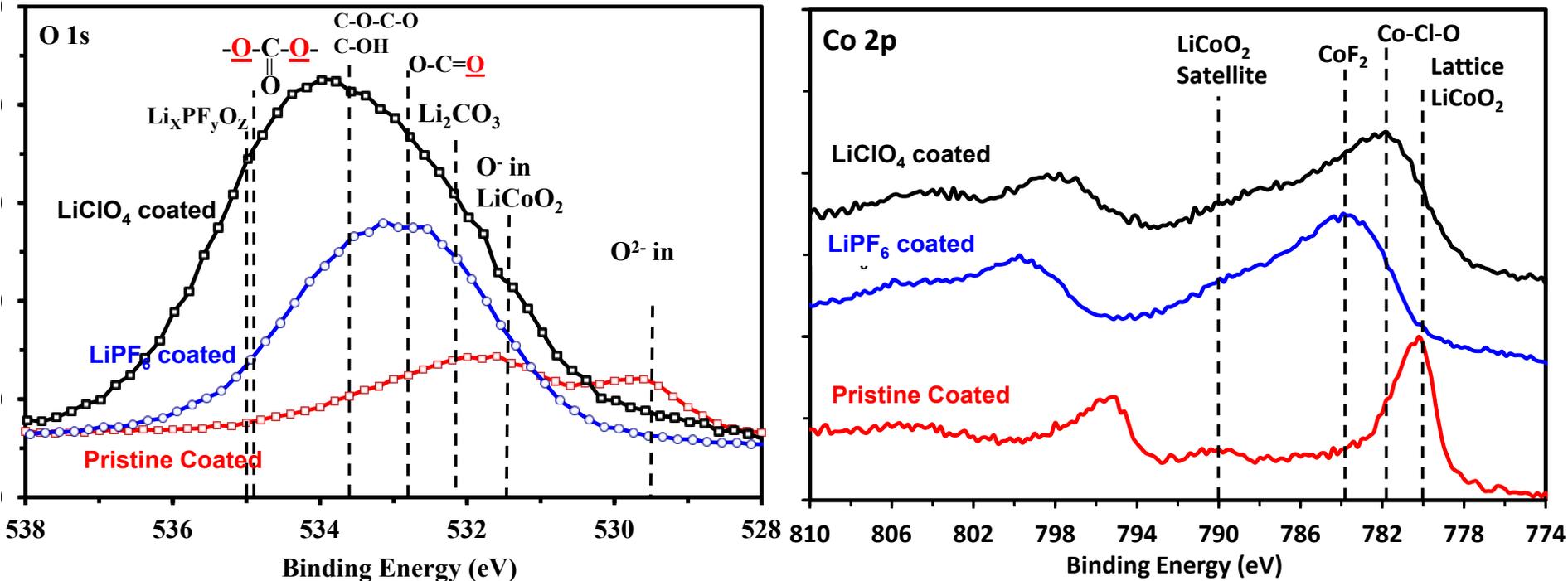


“ $\text{AlPO}_4$ ” coated  $\text{LiCoO}_2$   
2.5-4.6V, 1/5C, 4.6V hold for 4hrs



# Why doesn't "AlPO<sub>4</sub>" coating enhance capacity retention in LiClO<sub>4</sub>-based electrolyte?

## X-ray photoelectron spectroscopy



LiPF<sub>6</sub> → less organic decomposition  
LiClO<sub>4</sub> → more organic decomposition

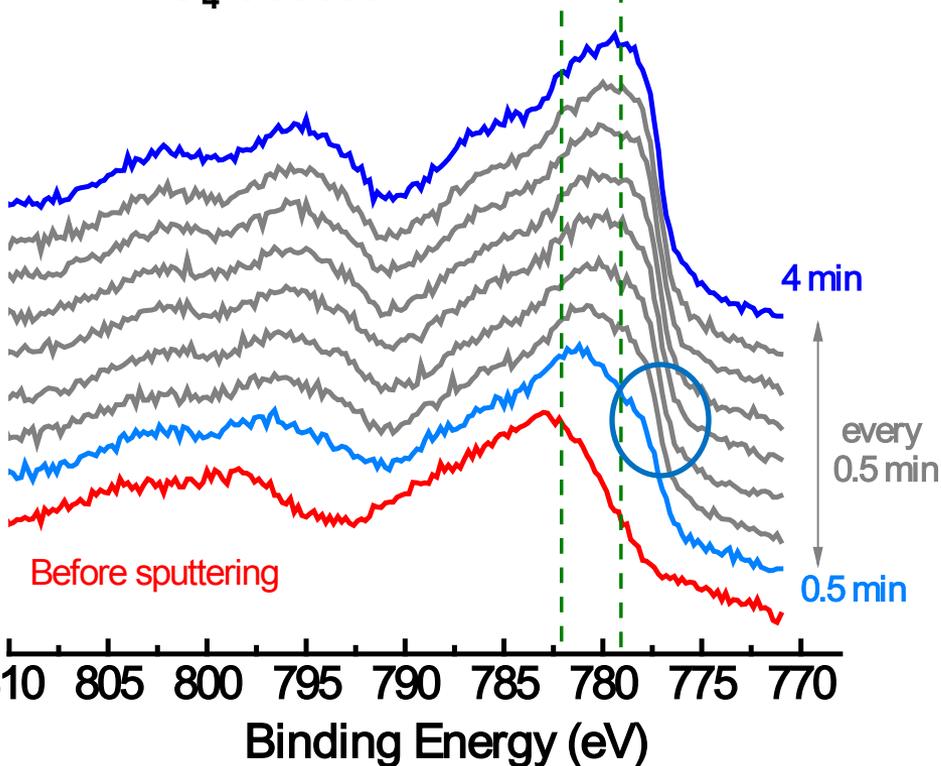
LiPF<sub>6</sub> → formation of CoF<sub>2</sub>  
LiClO<sub>4</sub> → no CoF<sub>2</sub>

**Formation of metal fluorides/oxyfluorides  
is key to enhance the cycle life.**

# X-ray photoelectron spectroscopy – depth profile

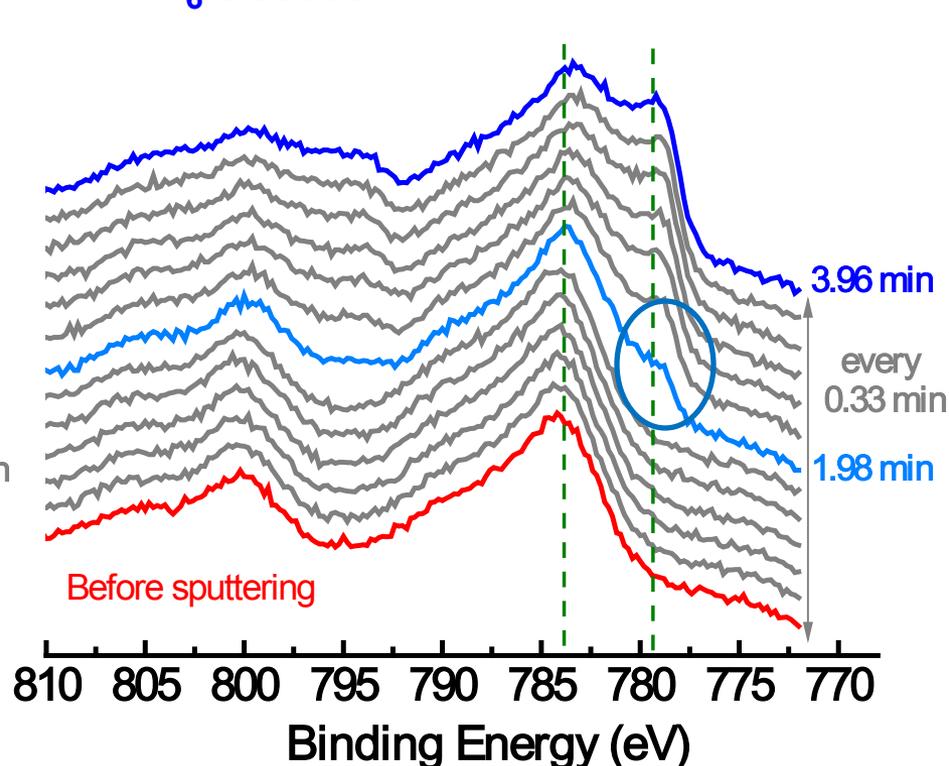
**LiClO<sub>4</sub> coated**

\* 30 Å SiO<sub>2</sub>/min



**LiPF<sub>6</sub> coated**

\* 30 Å SiO<sub>2</sub>/min



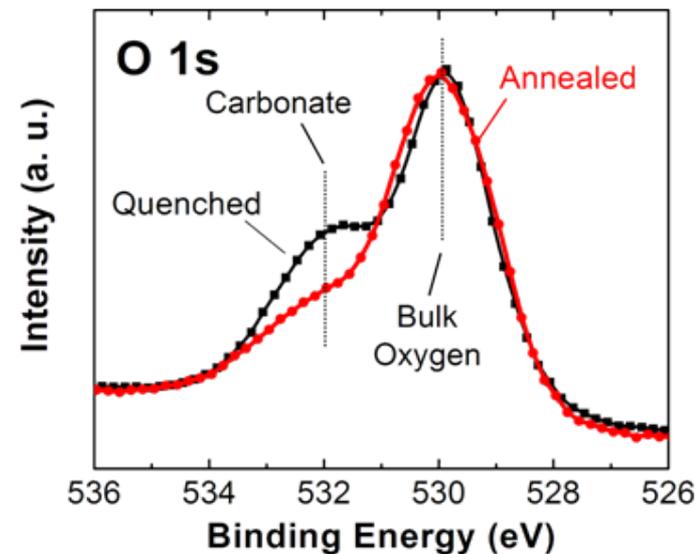
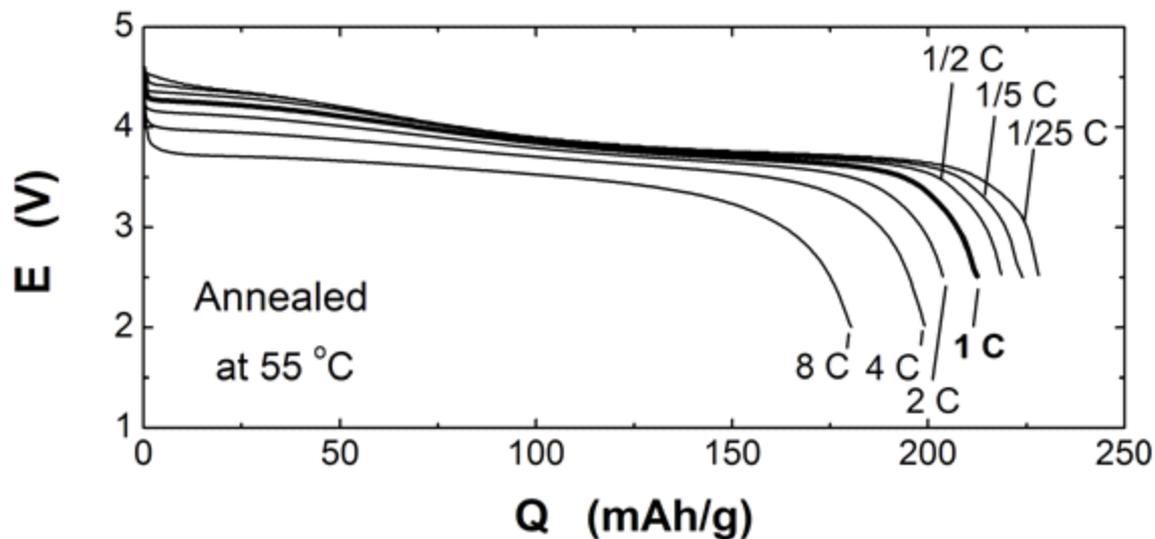
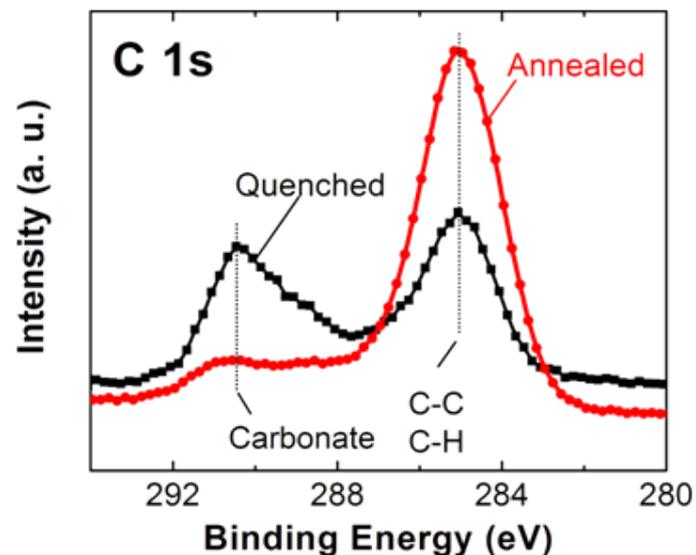
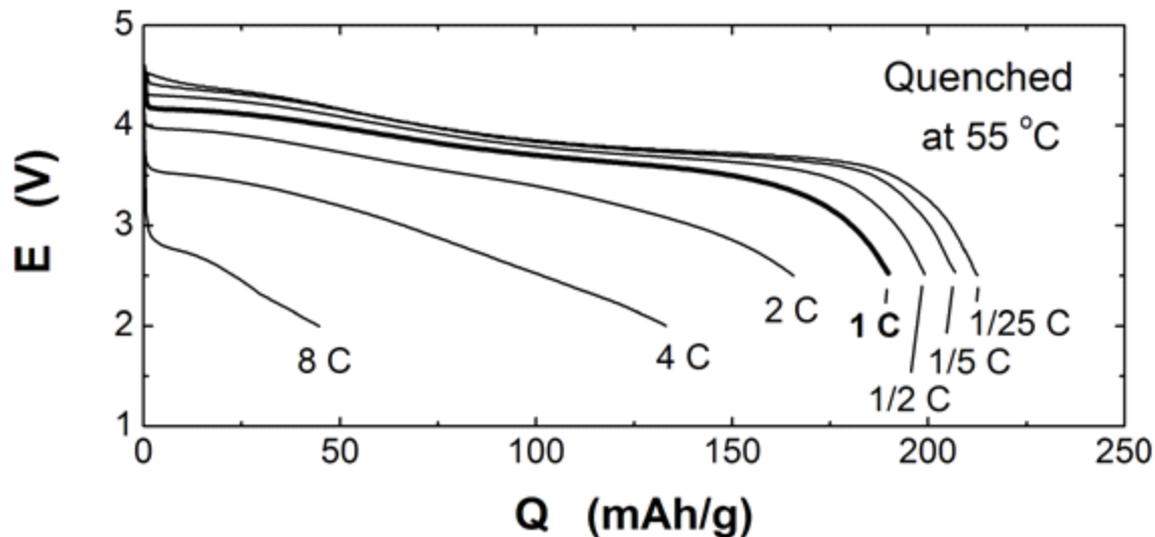
Bulk signal revealed after 0.5 min of sputtering

Bulk signal revealed after 2 min of sputtering

**Right thickness (~5-6 nm) is key for a stable solid-electrolyte interface**

# Technical Accomplishment (2010) – $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$

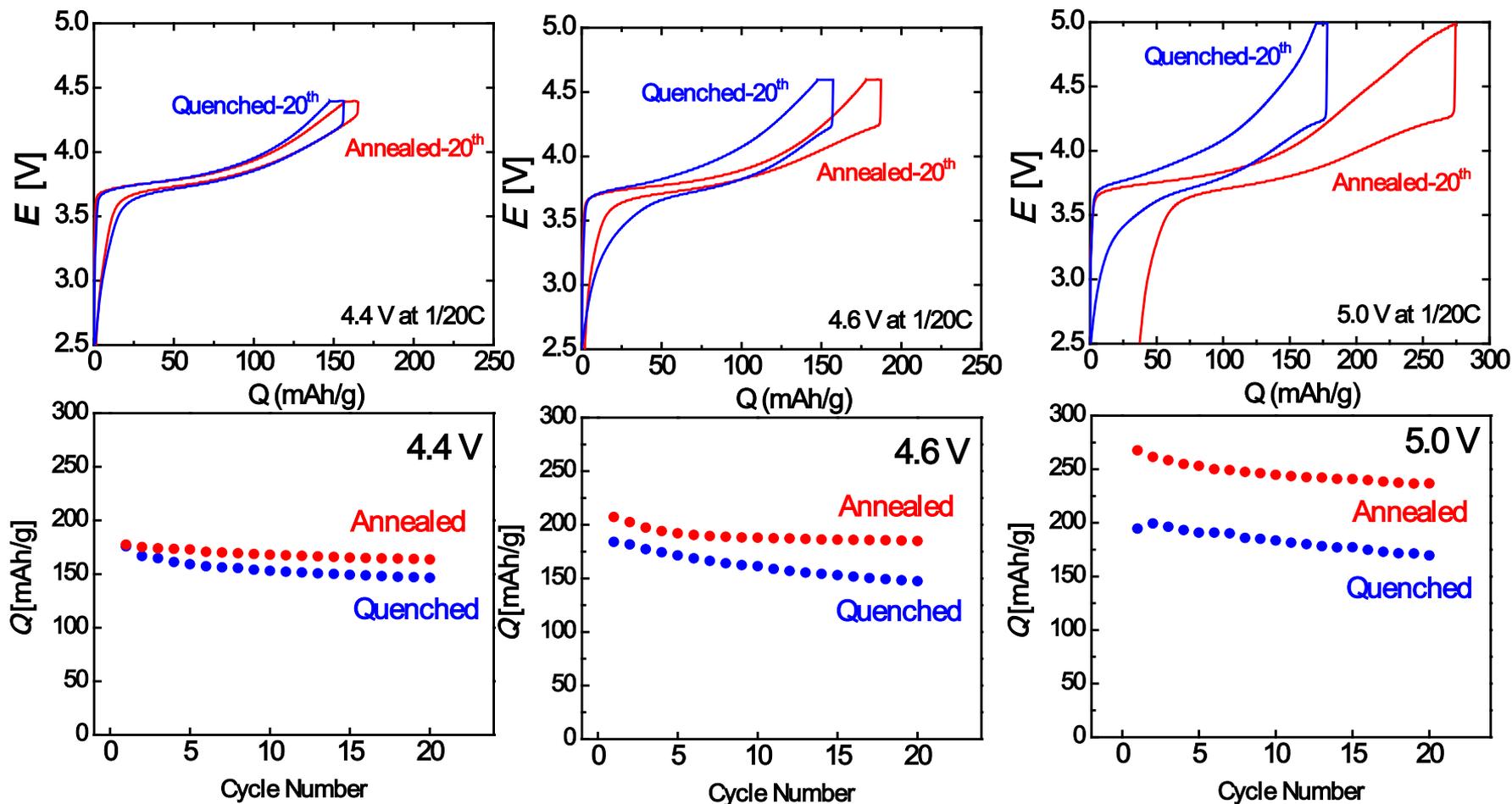
## Reduction of surface carbonates improves rate capability



N. Yabuuchi, Y.C. Lu, A.N. Mansour, T. Kawaguchi, and Y. Shao-Horn, *Electrochem. Solid-State Lett.*, **13**, A158-A161 (2010)

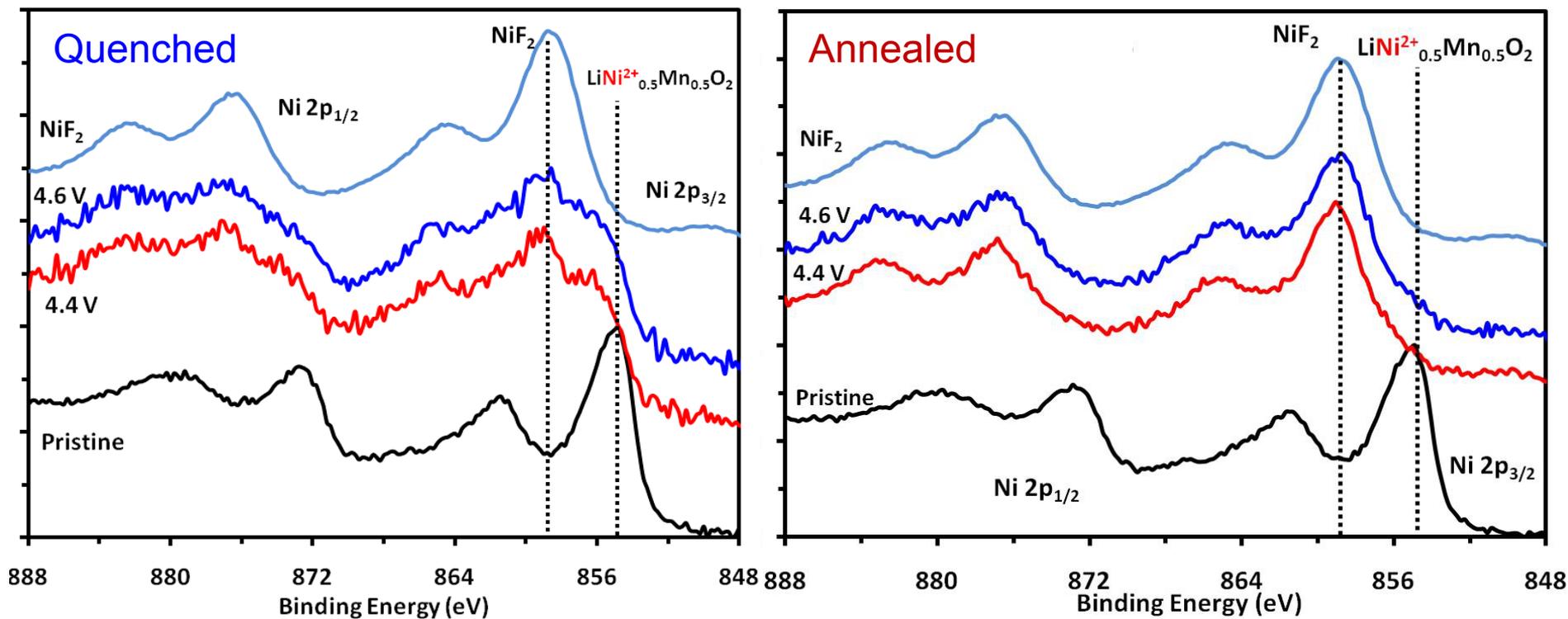
N. Yabuuchi, Y.C. Lu, A.N. Mansour, S. Chen, and Y. Shao-Horn, *J. Electrochem. Soc.*, **2**, A192-A200 (2011)

# Annealed $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ shows better cycling than quenched to high voltages



# NiF<sub>2</sub> found on cycled quenched & annealed LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>

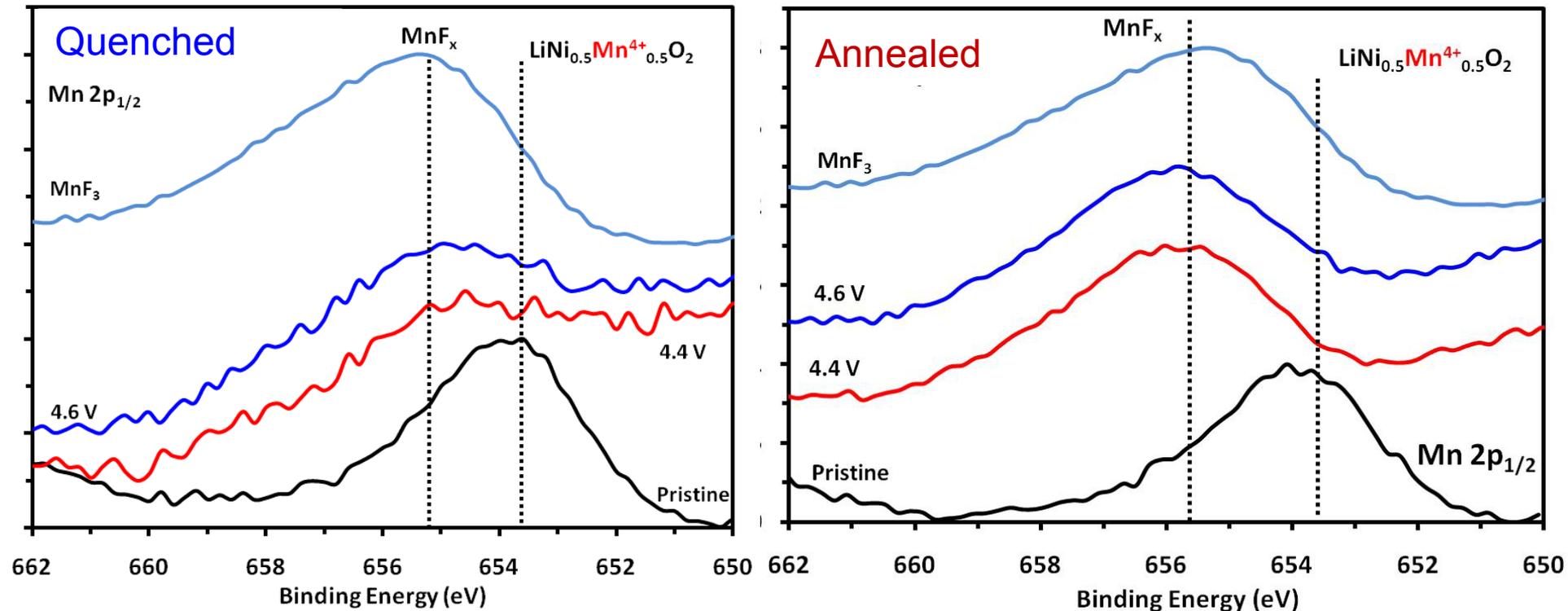
## X-ray photoelectron spectroscopy – Ni 2p



**Thicker (Ni, Mn)F<sub>x</sub> films formed on annealed electrodes**

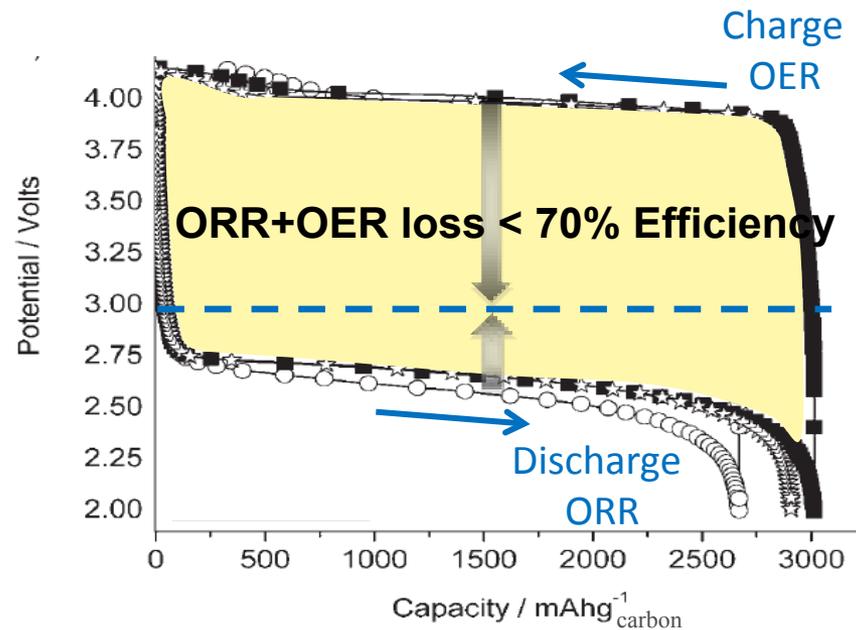
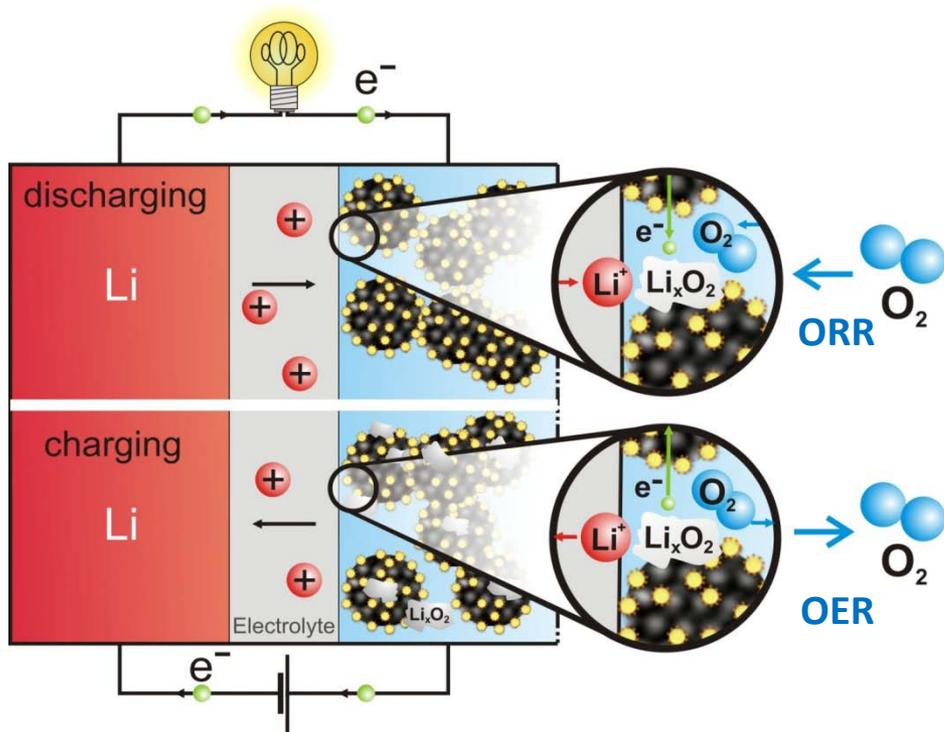
**MnF<sub>x</sub> was found on cycled quenched & annealed LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> but thicker films formed on annealed electrodes**

*X-ray photoelectron spectroscopy – Mn 2p<sub>1/2</sub>*



**Thicker (Ni, Mn)F<sub>x</sub> films formed on annealed electrodes**

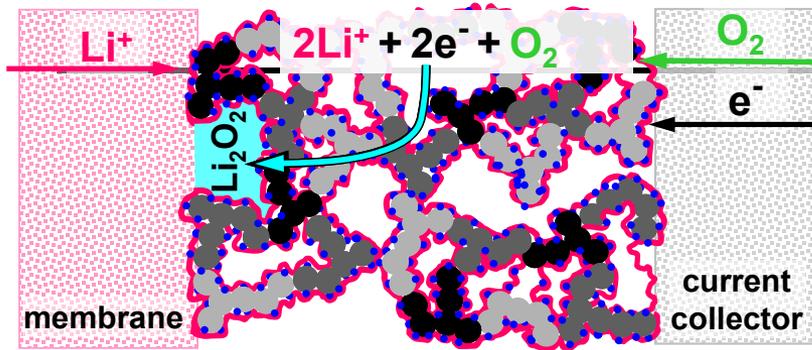
# Promoting the kinetics of lithium oxide electrodes with catalysts



A. Débart et al, *Angew. Chem. Int. Ed.* 47 (2008) 4521

## Large polarization observed in decomposing lithium oxides

# 3-5-fold in gravimetric energy of $\text{Li}_2\text{O}_x$ vs. Li-Ion batteries



assumptions:

$0.36 \text{ g}_{\text{carbon}}/\text{cm}^{3*}$ , 15%  $\epsilon_{\text{carbon}}$ , 25%  $\epsilon_{\text{electrolyte}}$ , 60%  $\epsilon_{\text{Li}_2\text{O}_x}$

	$\text{Li}_2\text{O}_2$	$\text{Li}_2\text{O}$	$\text{LiCoO}_2$
$Q_s$ wrt. C [mAh/g <sub>carbon</sub> ]	4600	6000	
$Q_s$ wrt. C+ $\text{Li}_2\text{O}_x$ [mAh/g <sub>(C+Li2Ox)</sub> ]	900	1350	160
average discharge voltage [V]	2.75	2.75	3.9
$E_s$ wrt. C+ $\text{Li}_2\text{O}_x$ [Wh/kg <sub>(C+Li2Ox)</sub> ]	2450	3700	620

\*W. Gu, D.R. Baker, Y. Liu, H.A. Gasteiger, in: *Handbook of Fuel Cells* (eds.: W. Vielstich et al.); Wiley (2009): vol. 6, p 631



Li-Air

Estimated gravimetric energy  
 ~ **3000 Wh/kg**<sub>Li2Ox-cathode</sub>

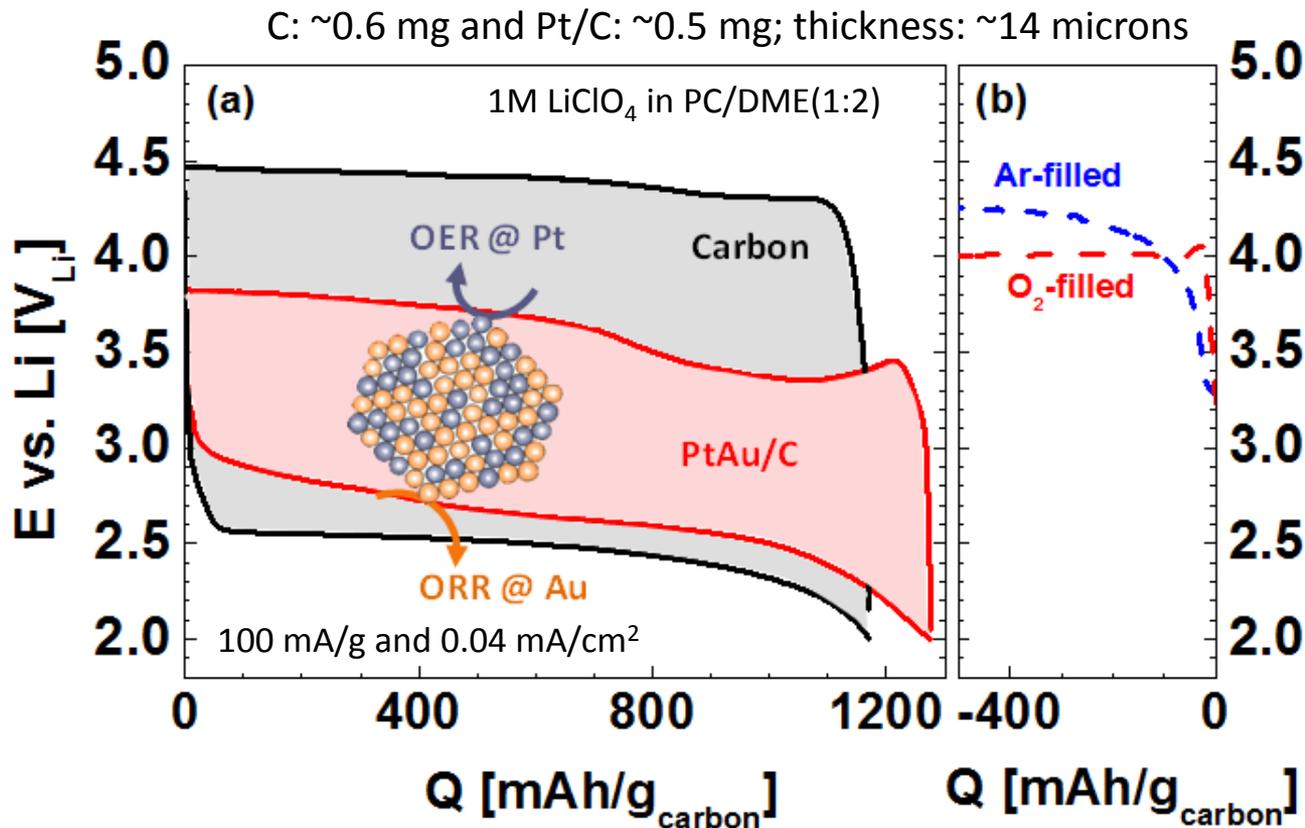
Projecting on the cell level – 1/3  
 ~ **1000 Wh/kg**<sub>Li-air cell</sub>

Li-Ion ( $\text{LiCoO}_2$ )

Estimated gravimetric energy  
 ~ **620 Wh/kg**<sub>LiCoO2-cathode</sub>

Projecting on the cell level – 1/3  
 ~ **210 Wh/kg**<sub>LiCoO2 cell</sub>

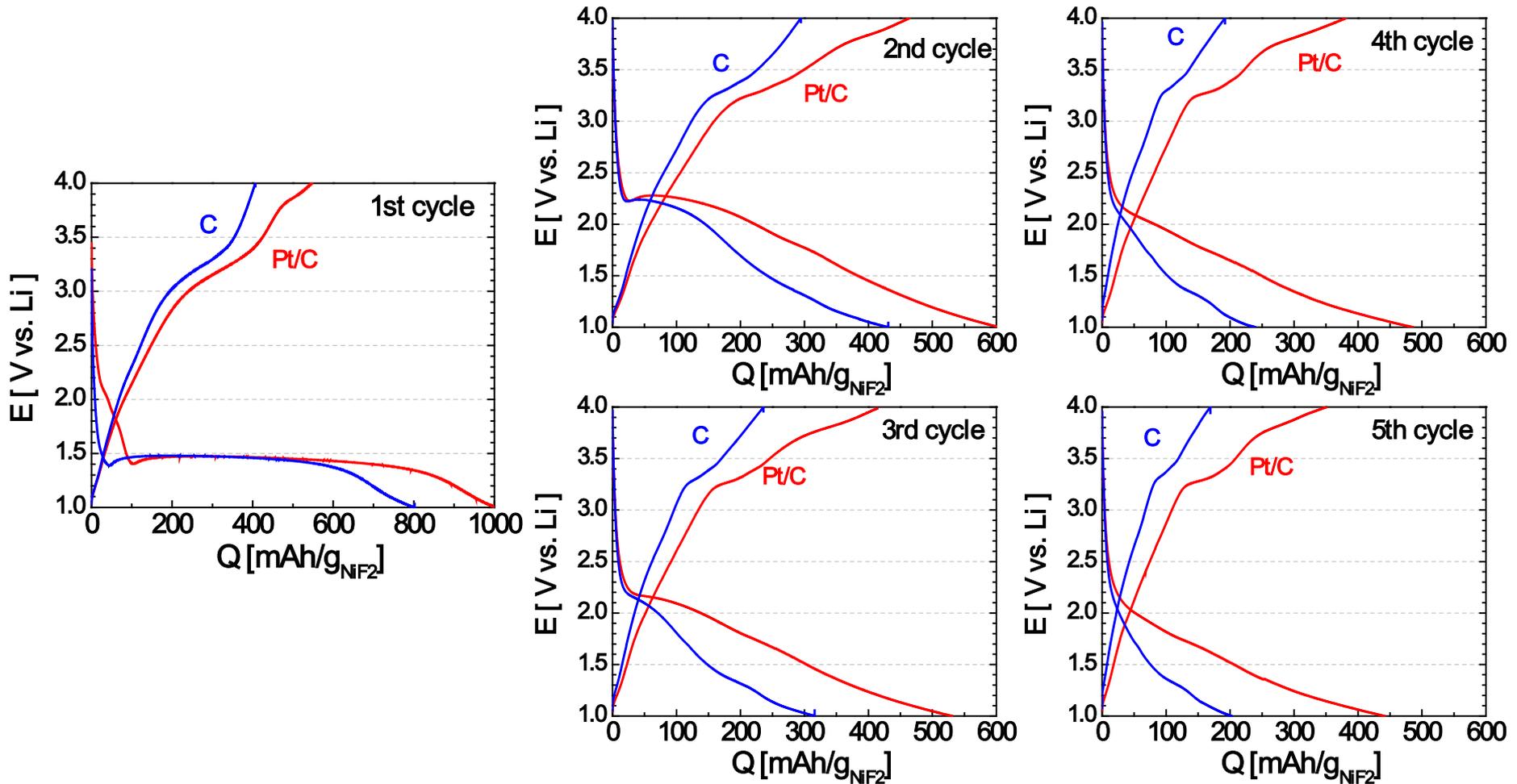
# PtAu/C exhibits record round-trip efficiency to date



**Achieved Round-trip efficiency: 75%**

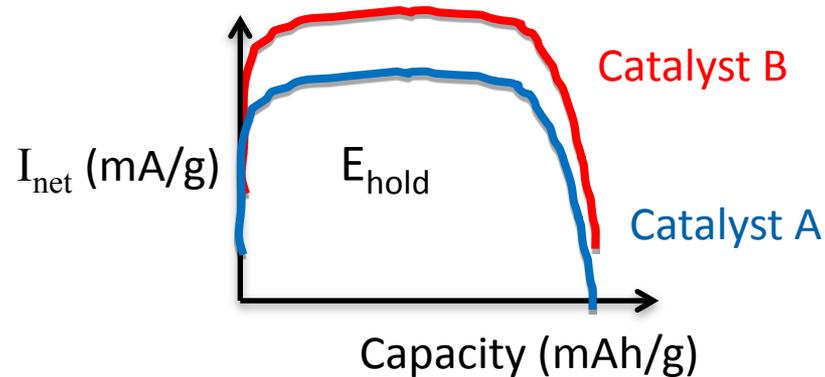
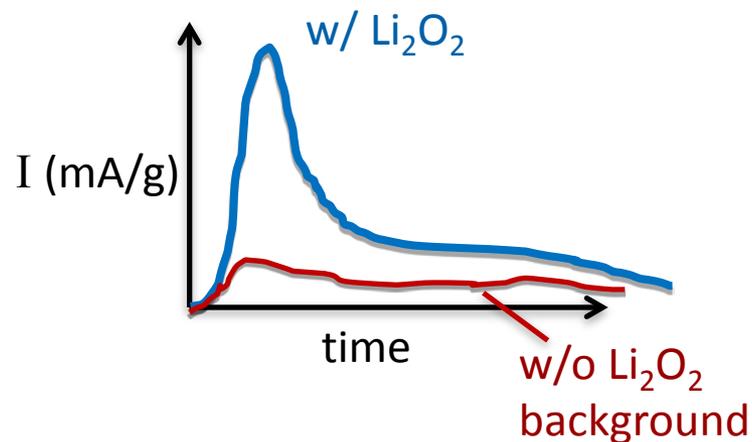
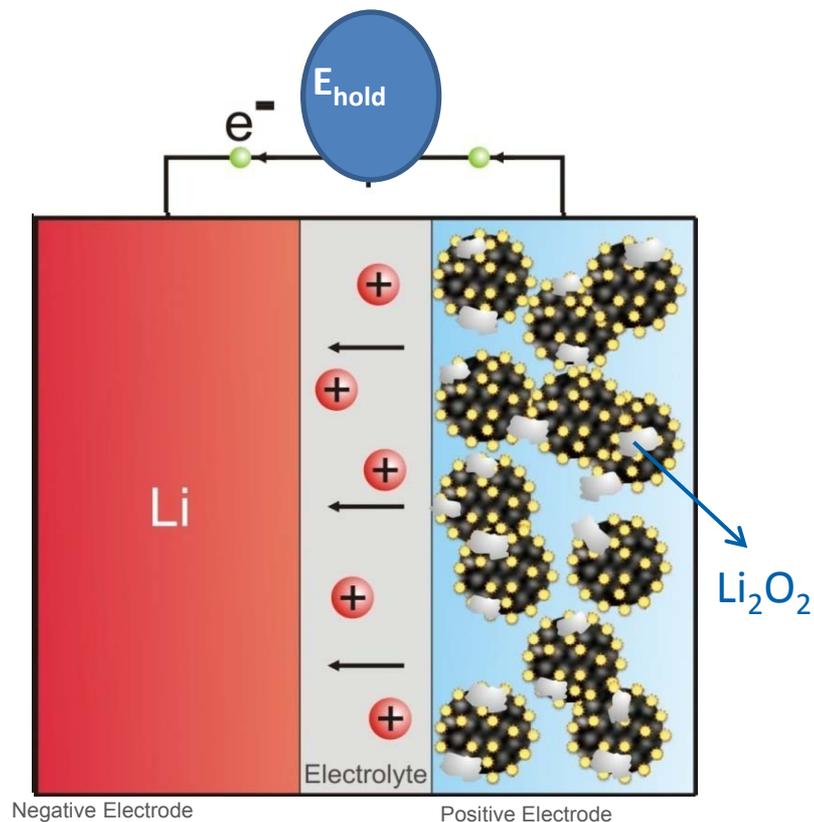
**What is the origin for the high bifunctional activity?**

# Catalyst effects on lithium metal-fluoride batteries



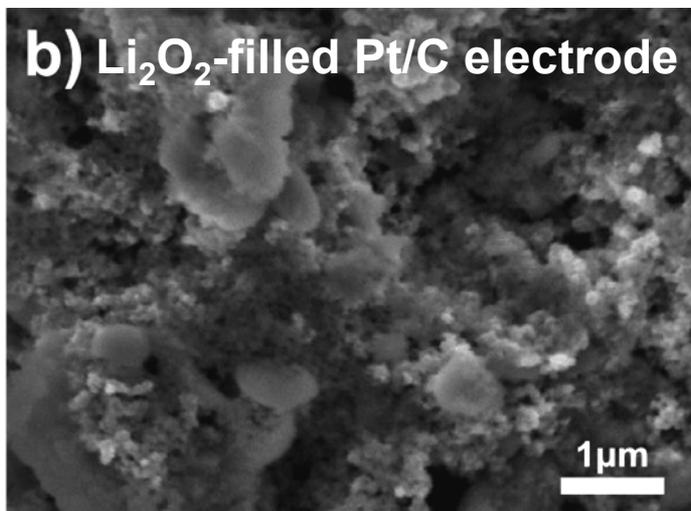
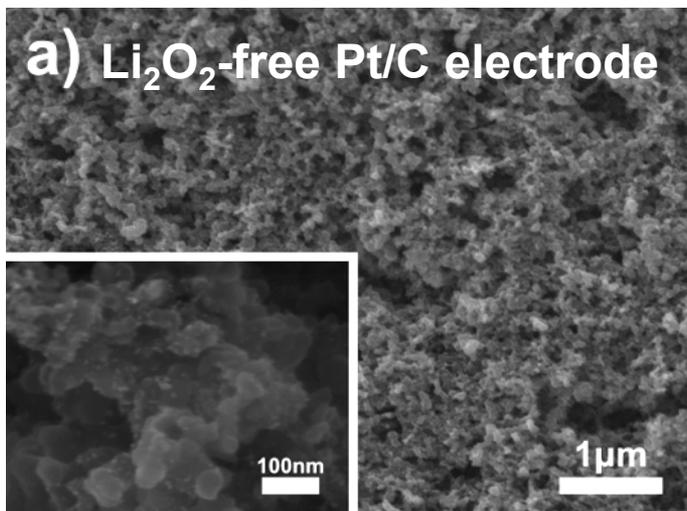
Catalyst effects present upon cycling

# $\text{Li}_2\text{O}_x$ -filled composite electrodes to quantify the oxygen evolution reaction (OER) activity

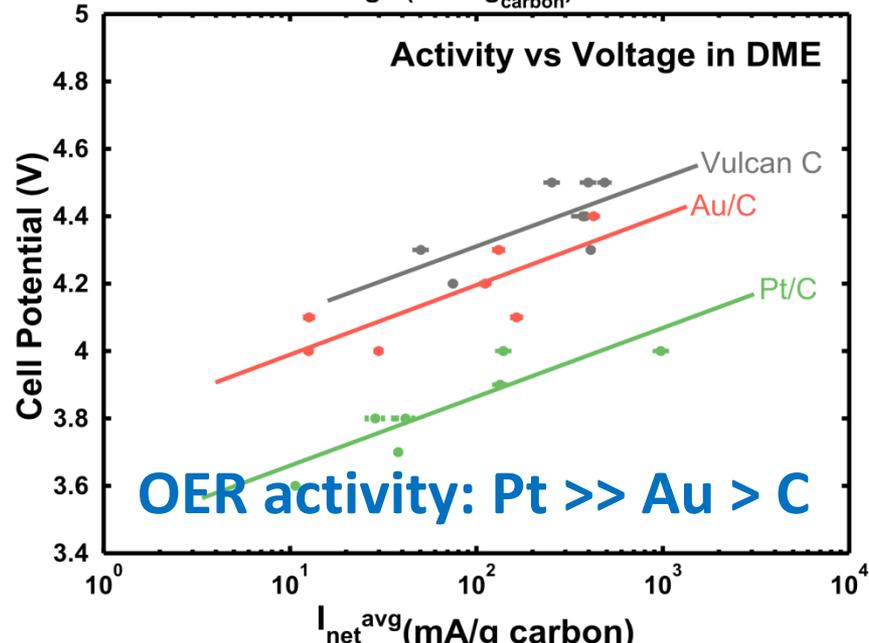
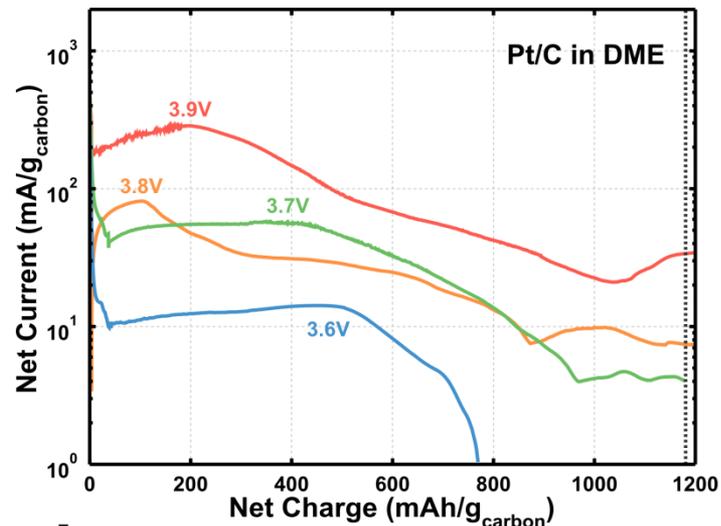


# OER activity of Pt nanoparticles was examined by $\text{Li}_2\text{O}_2$ -filled composite electrode

Scanning electron microscopy

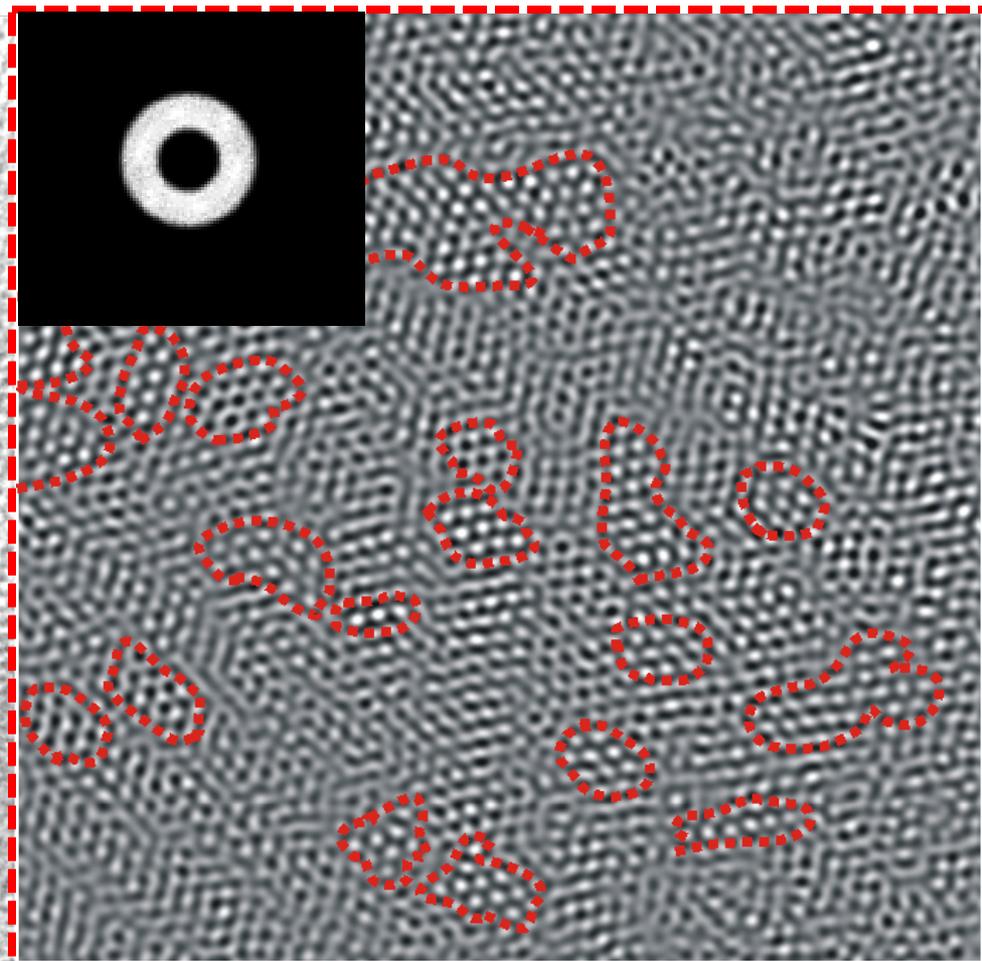
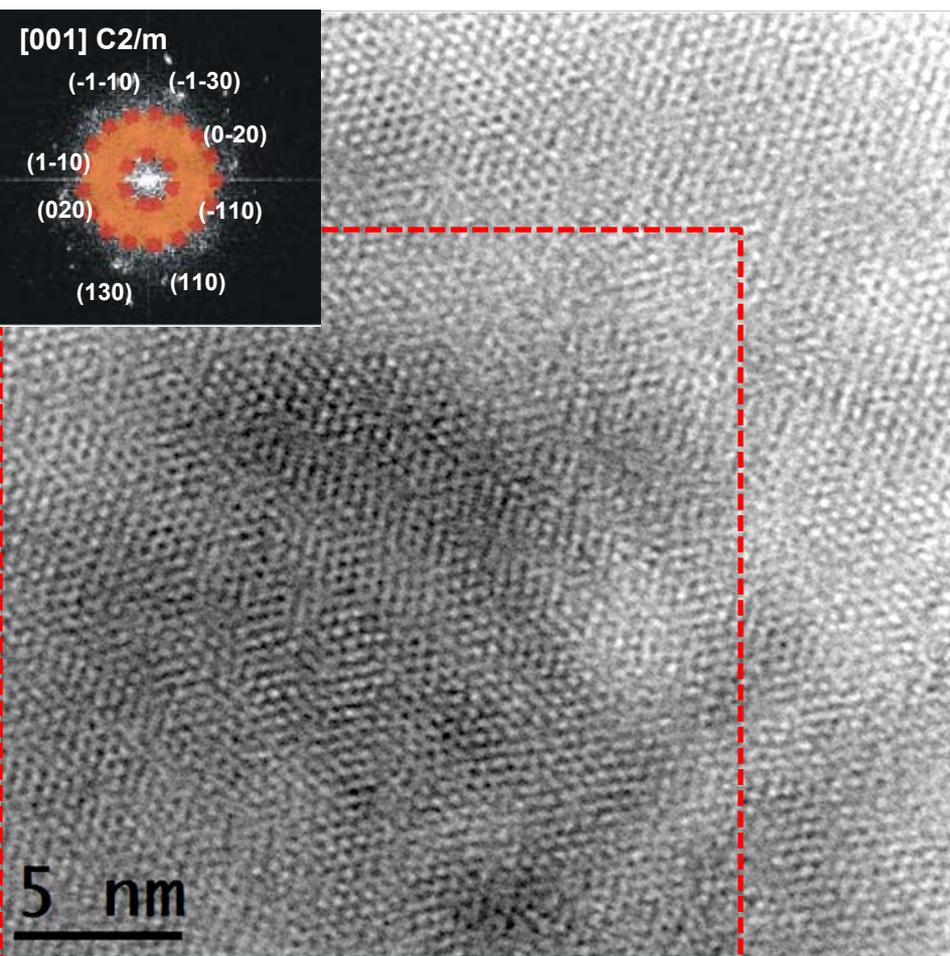
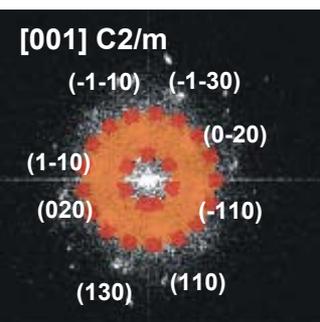


Potentiostatic test of  $\text{Li}_2\text{O}_2$ -filled Pt/C electrode



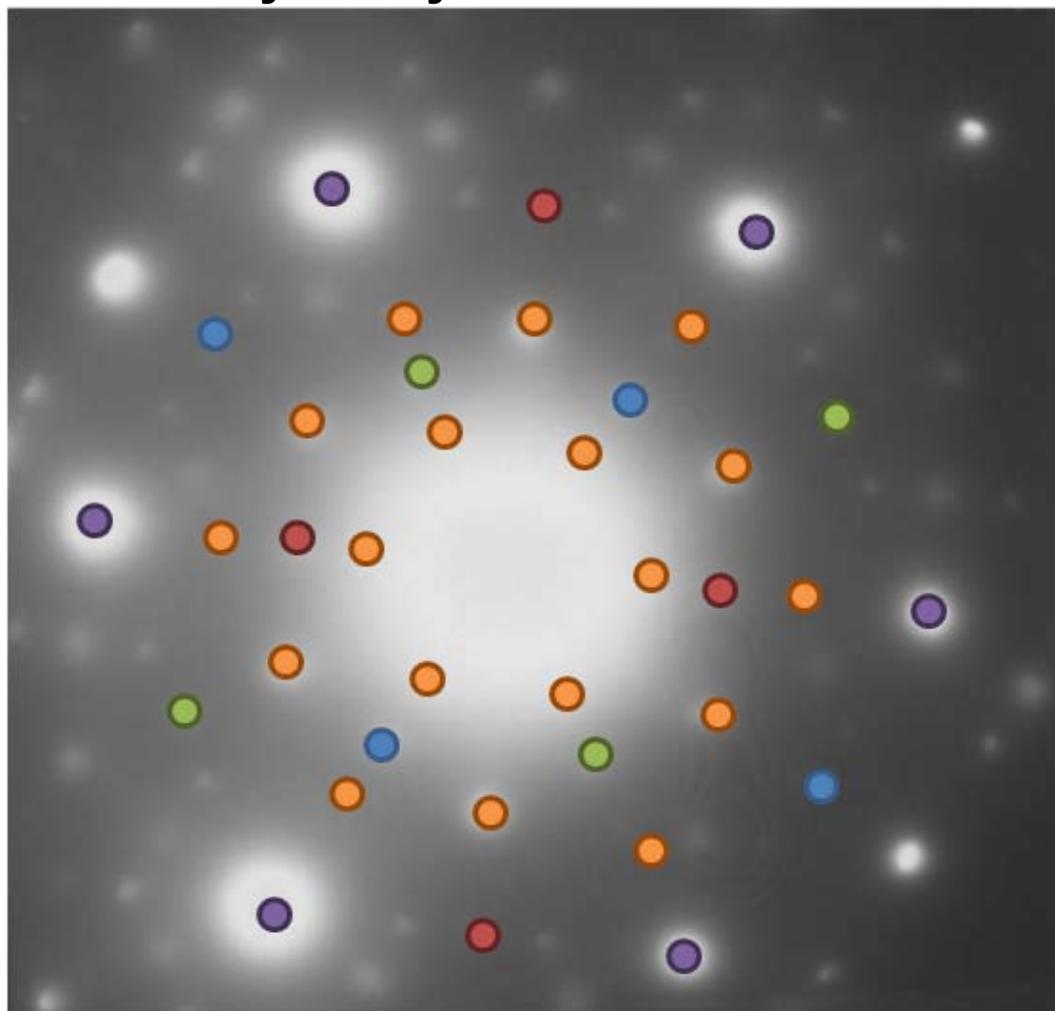
# Collaboration with S.H. Kang and M.M. Thackeray

Fourier filtering of pristine  $0.5\text{Li}_2\text{MnO}_3+0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$  layered-layered composite cathode revealed evidence of monoclinic  $\text{Li}_2\text{MnO}_3$  nanodomains



## Collaboration with S.H. Kang and M.M. Thackeray

Diffraction patterns of cycled  $0.5\text{Li}_2\text{MnO}_3 + 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$  layered-layered composite cathode reveal integration between several different crystal symmetries and orientations



The electron diffraction pattern reveals integration between hexagonal  $\text{LiMO}_2$ , super-lattice ordered hexagonal  $\text{LiMO}_2$  and 3-different orientations of monoclinic  $\text{Li}_{0.5}\text{MnO}_2$

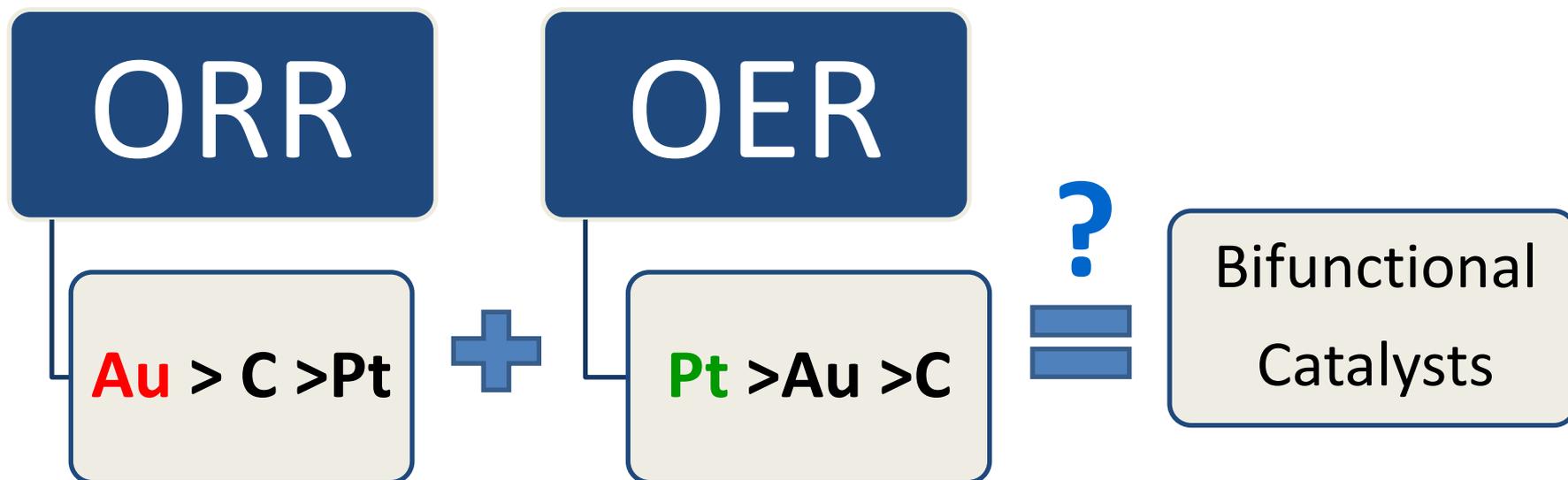
# Ongoing and Planned Activities

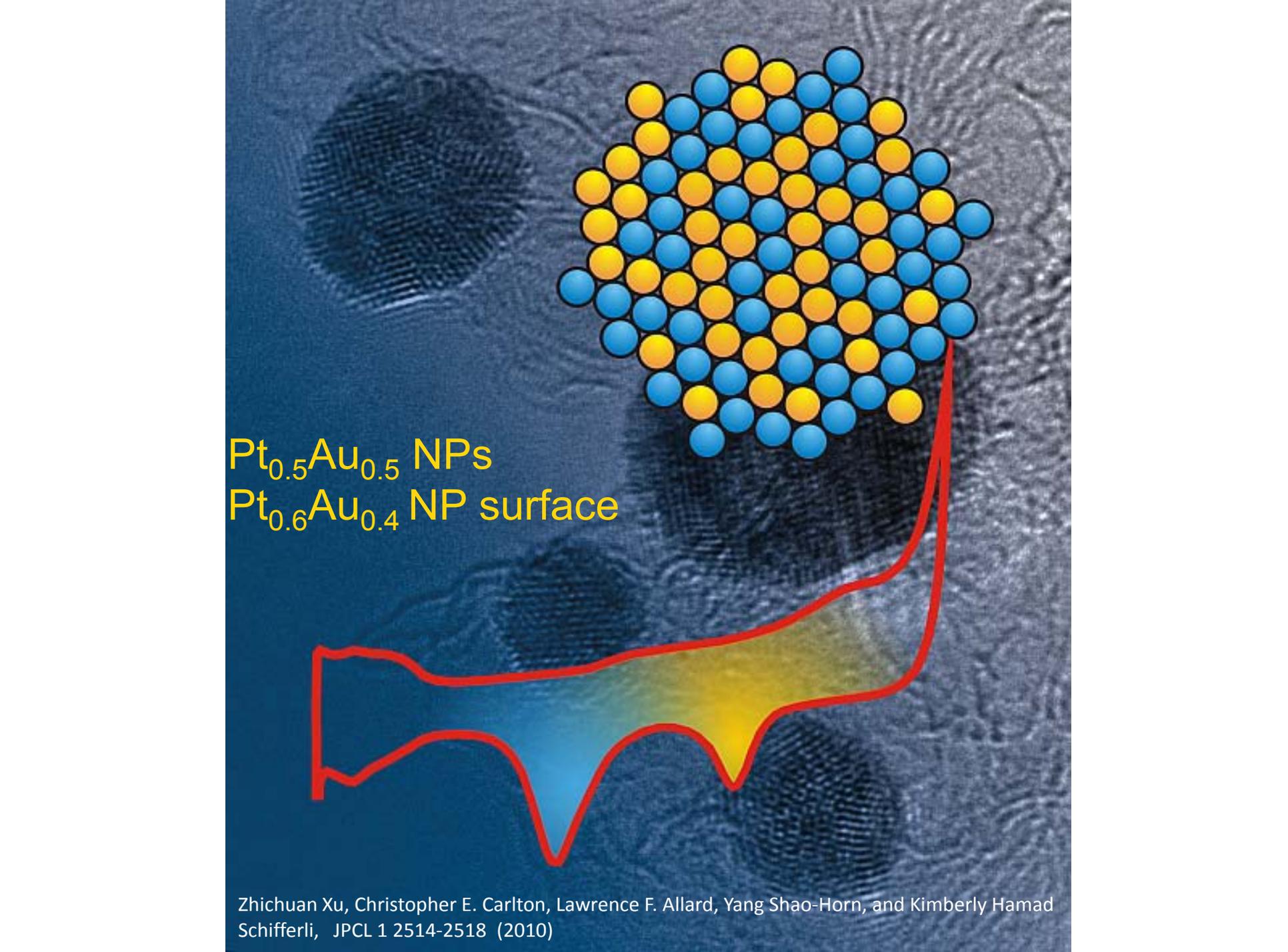
- **Continue to examine the role of surface chemistry on cycle life and rate capability of low cost and high energy positive electrode materials such as  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  using angle-resolved XPS and electron yield XAS:**
  - **Examine variations in the surface chemistry of cycled  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  electrodes. In this case, the electrodes will be transferred from an Ar filled glove box to the analysis chamber of the XPS system without exposure to ambient conditions.**
- **Continue to develop high-energy electrode materials  $\text{Li}_2\text{O}_x(\text{MO}_y)_z$  electrodes (M = nonnoble metal transition metals) and examine the reaction mechanisms**
  - **Examine the catalyst effects on the decomposition rate of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  in composite electrodes of  $\text{Li}_2\text{O}_x(\text{MO}_y)_z$  by systematic potentiostatic tests, SEM, XPS, Raman, FT-IR and XRD characterization.**

# Contact information

**Yang Shao-Horn at 617 253-2259**  
**shaohorn@mit.edu**

**Au** is the most active for ORR and **Pt** is the most active for OER among Au, Pt, C





$\text{Pt}_{0.5}\text{Au}_{0.5}$  NPs  
 $\text{Pt}_{0.6}\text{Au}_{0.4}$  NP surface

# Examine the effects of sample washing on XPS analysis

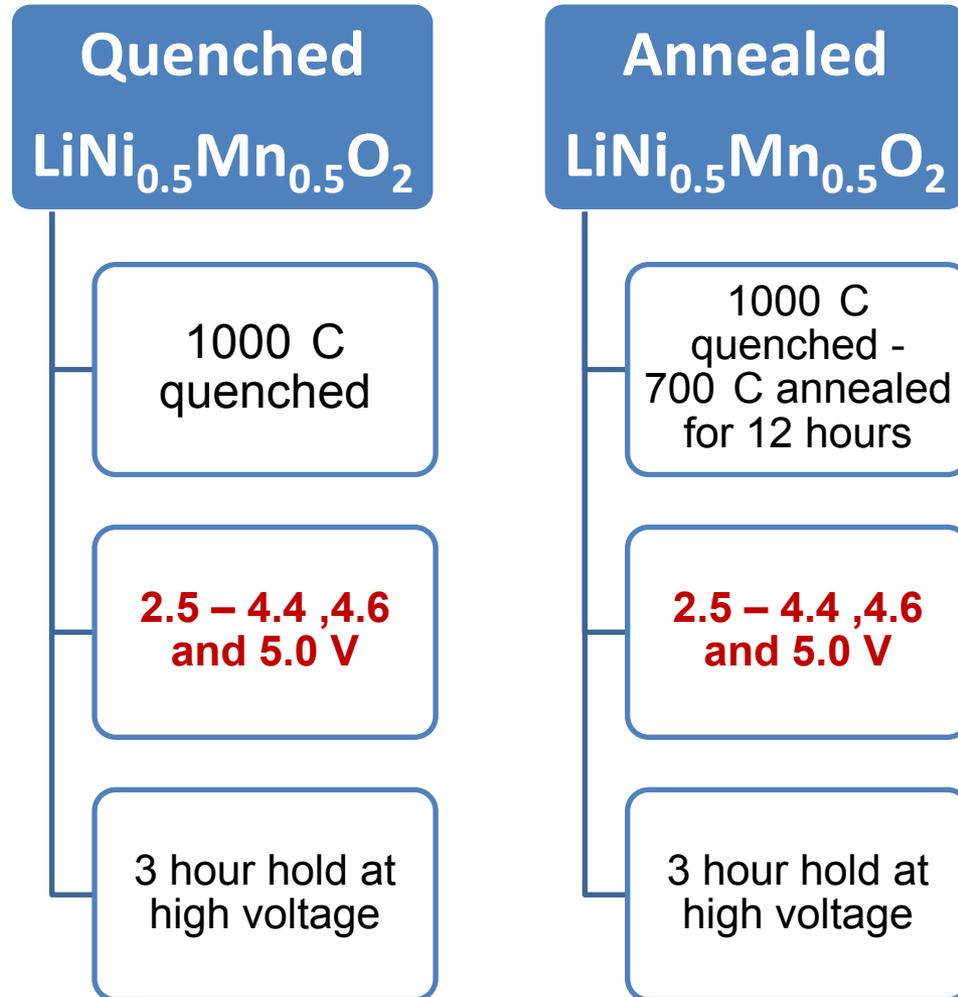
Typical XPS analysis procedure for cycled electrodes

Sample is **washed** with solvent prior to XPS analysis

Our XPS analysis procedure for cycled electrodes

**No** wash step or any pretreatment prior to XPS analysis

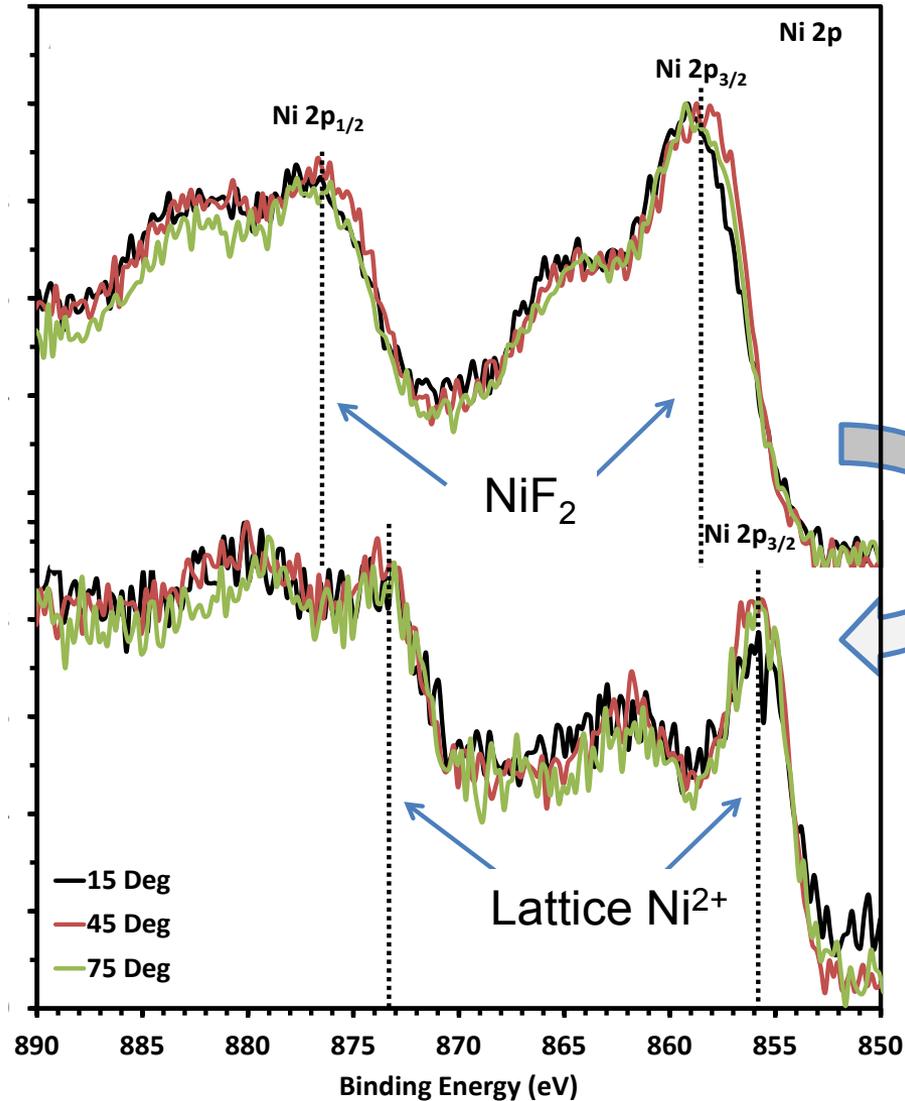
# Search for ideal surface chemistries for long cycle life under high voltage operation



# Washing step removes the metal fluoride/oxyfluoride

## Angle resolved X-ray photoelectron spectroscopy – Ni 2p

Annealed  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  cycled in  $\text{LiPF}_6$

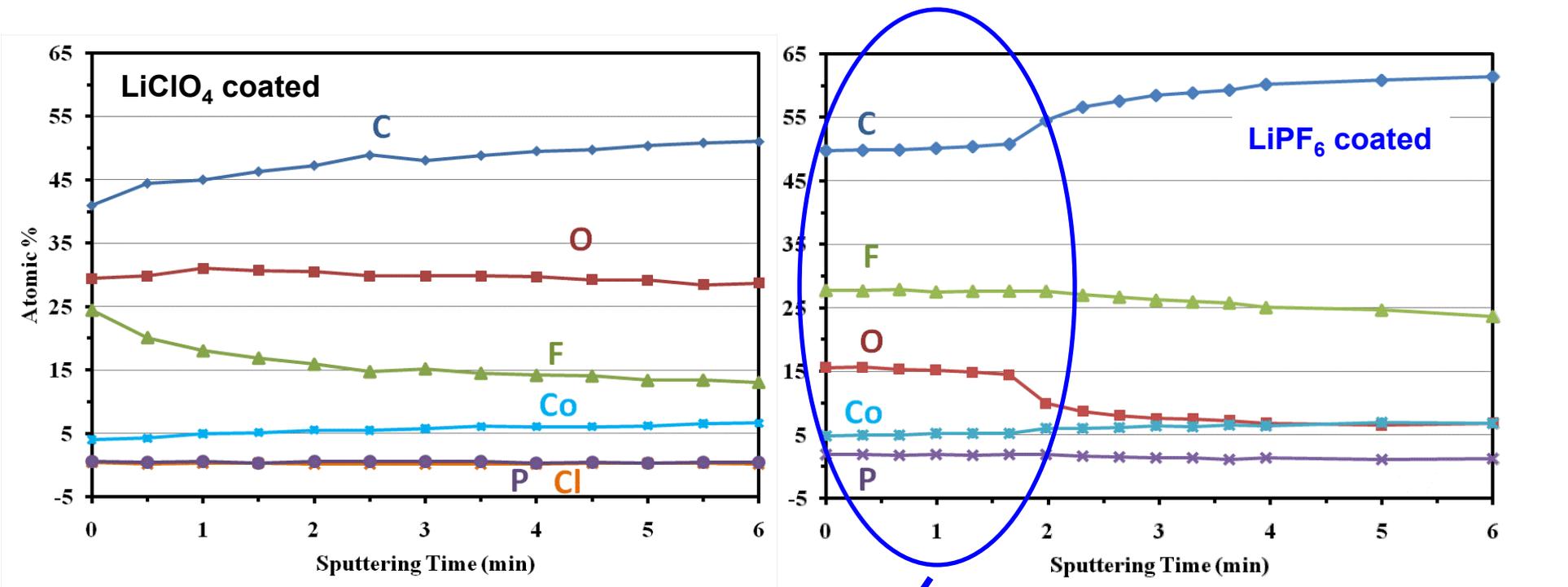


After rinsed in  
DMC for 2 min

**A desired solid-electrolyte interface consists of :**

- **Right chemistry** → metal fluoride / oxyfluoride
- **Right thickness** → ~ 5-6 nm

*X-ray photoelectron spectroscopy – sputtering profile*

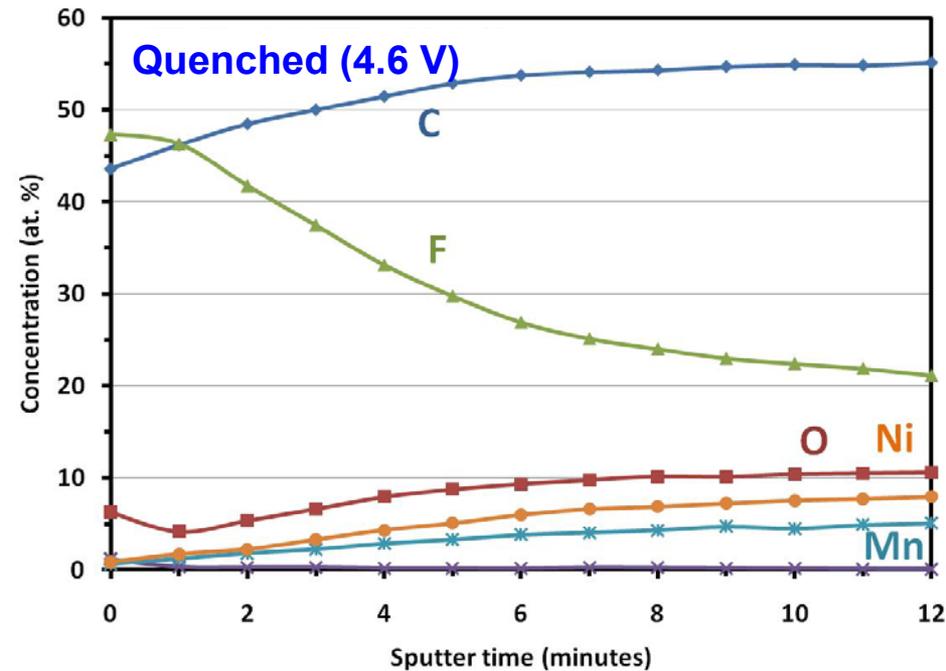


**2 min of flat sputtering profile indicates  
→ A stable film with a substantial thickness**

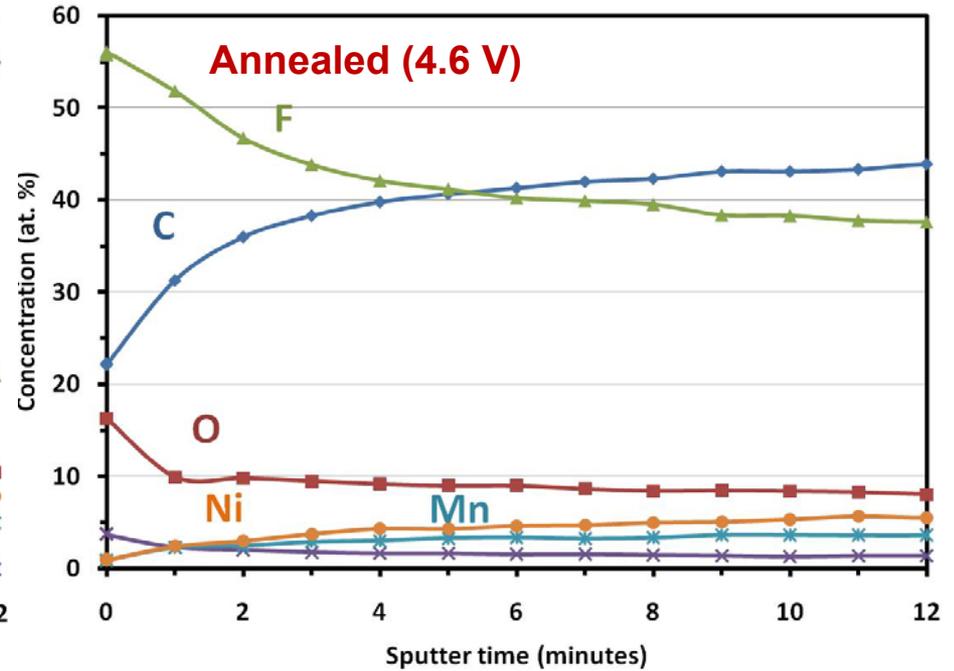
# Cycled annealed electrode is dominated by F-chemistry

# Cycled quenched electrode is dominated by C & F-chemistry

## *X-ray photoelectron spectroscopy – sputtering profile*



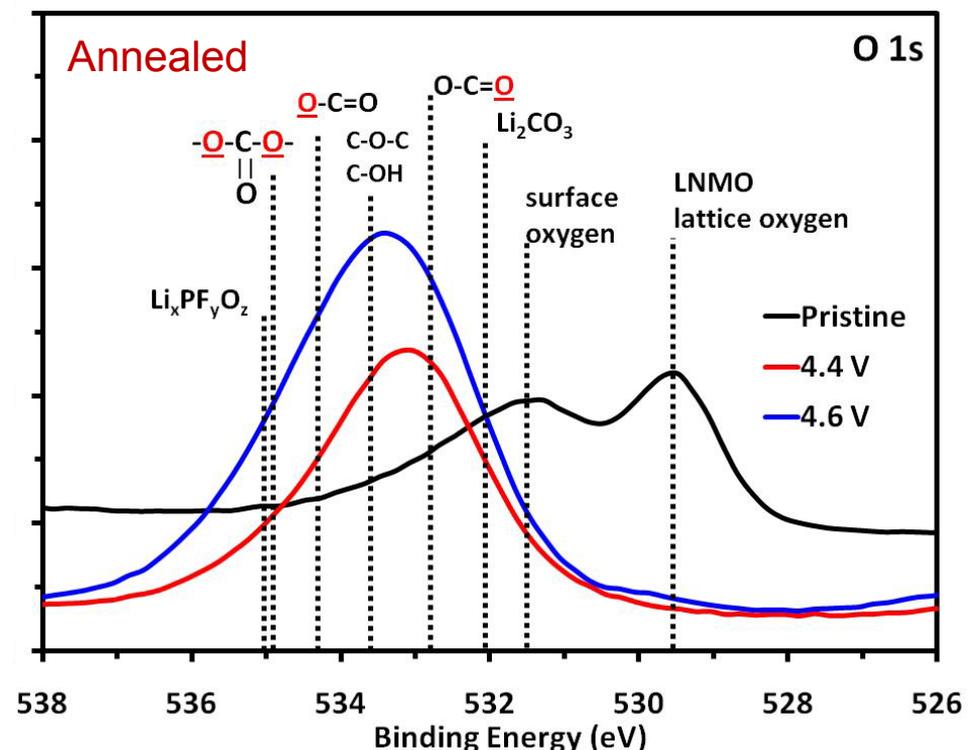
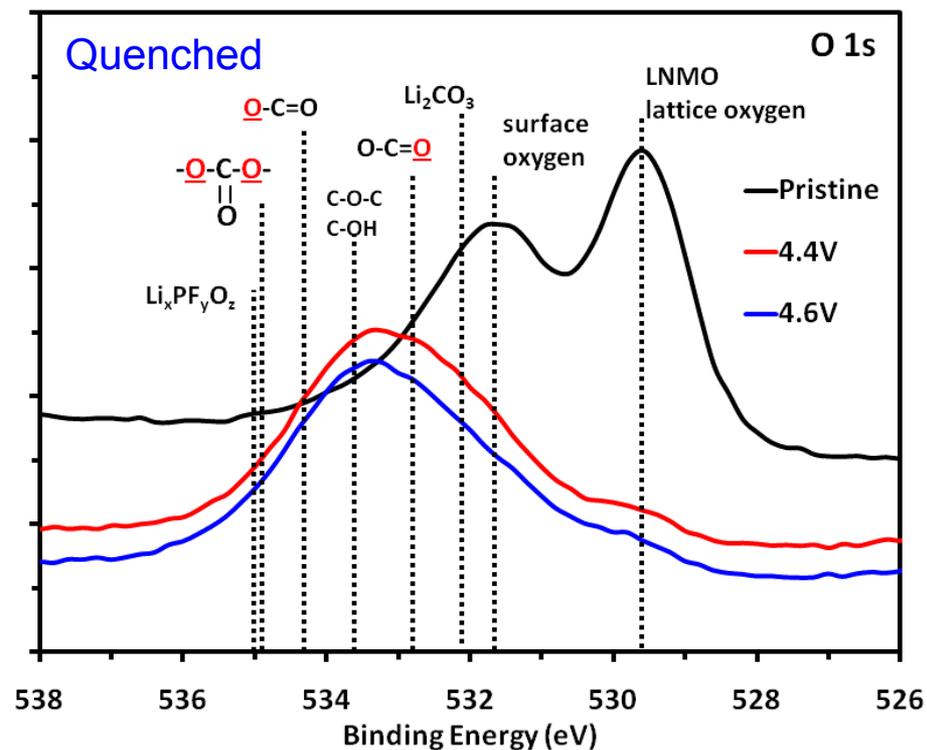
F/C ratio = 1.1



F/C ratio = 2.5

# O 1s spectra confirm that thicker film is formed on cycled annealed electrode compared to cycled quenched electrode

## X-ray photoelectron spectroscopy – O 1s



- Lattice oxygen signal is visible, suggesting thinner film formation

- Lattice oxygen signal is not visible, suggesting thicker film formation

# Pt was shown to have the highest OER activity among Pt, Au and C

*Activity vs cell potential*

